

Oxygen Reduction on a Carbon-based Gas Diffusion Electrode in Non-aqueous Electrolyte for Li-air Batteries

Deyang Qu

University of Massachusetts Boston

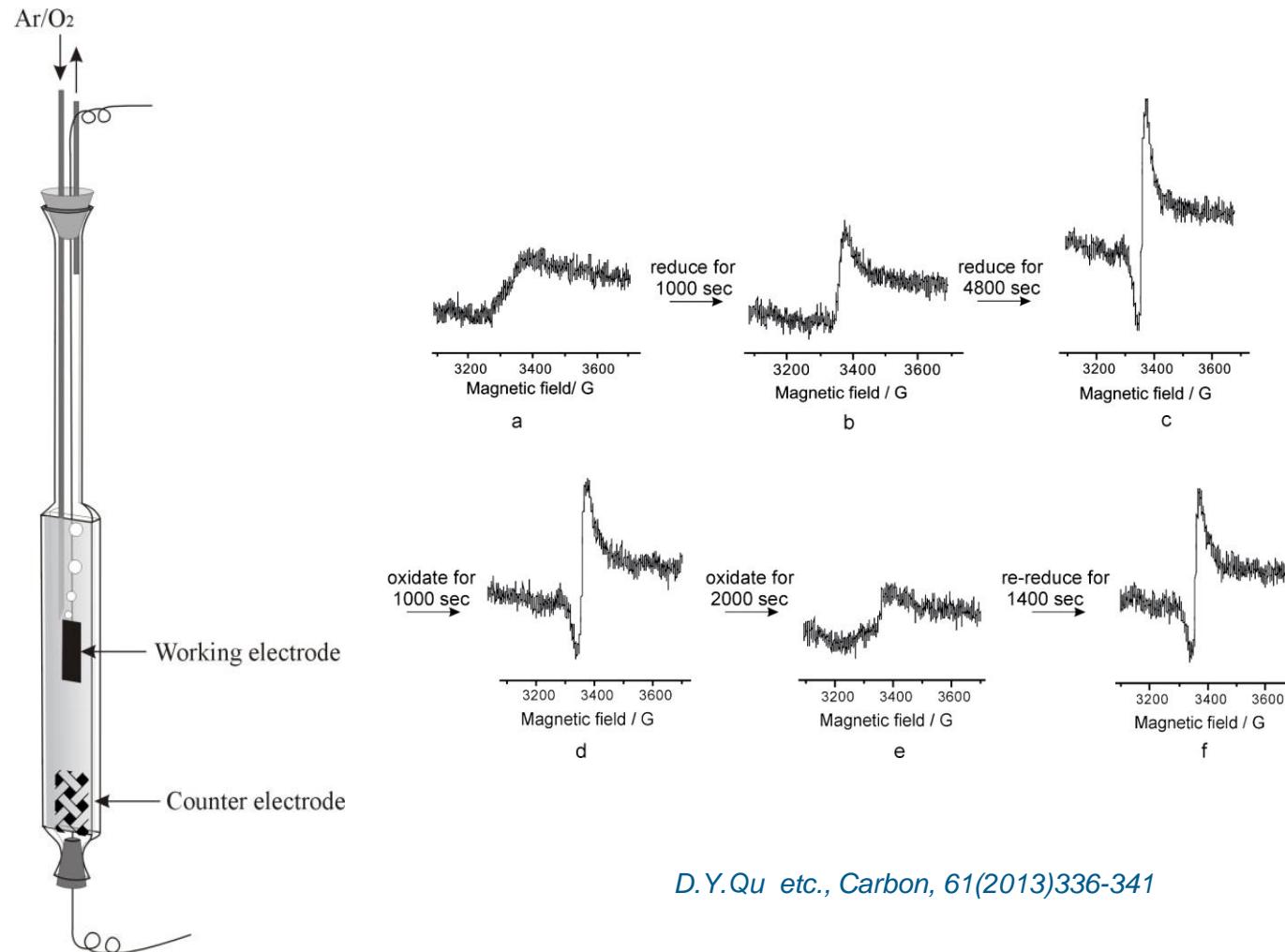
Xiao-Qing Yang

Brookhaven National Laboratory

Obstacles for Li-air chemistry

- ▶ Interaction between superoxide ($O_2^{-\cdot}$) with organic solvents.
- ▶ Rechargeability.
- ▶ Round-trip efficiency – can catalyst help or else?
- ▶ Solid products (e.g. Li_2O) deposition, which causes premature passivation of the gas diffusion electrode.
- ▶ Oxygen solubility and diffusion rate, which determine the oxygen reduction rate thus the discharge rate of Li-air batteries.
- ▶

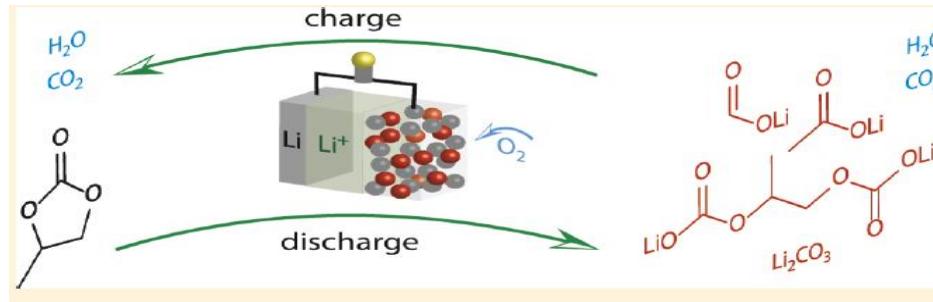
In-situ EPR Spectro-electrochemical Studies Proved the Formation of O_2^- During O_2 Reduction



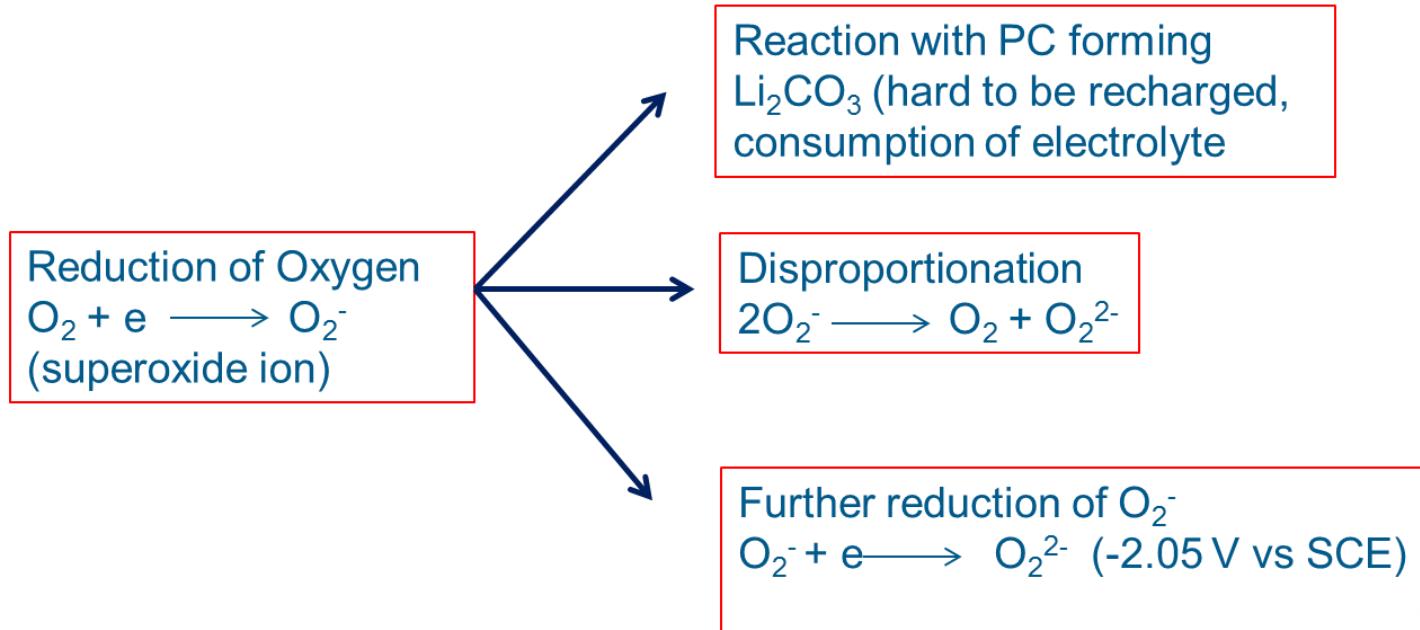
D.Y.Qu etc., Carbon, 61(2013)336-341

Superoxide can react with PC

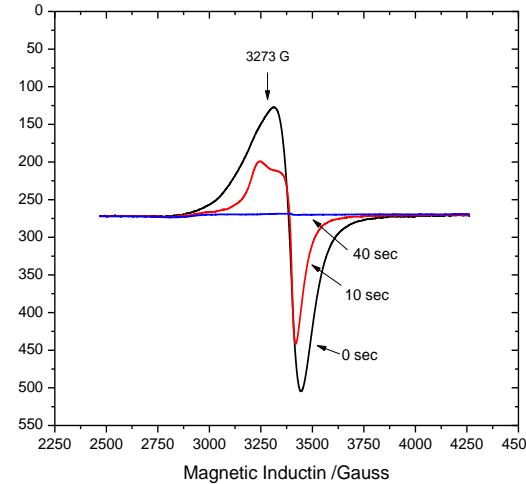
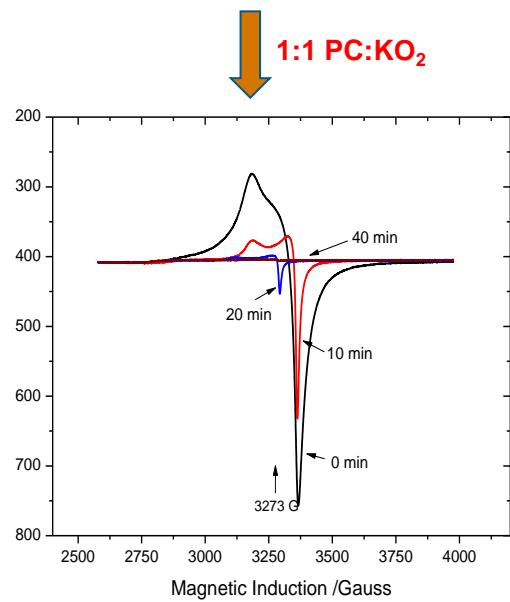
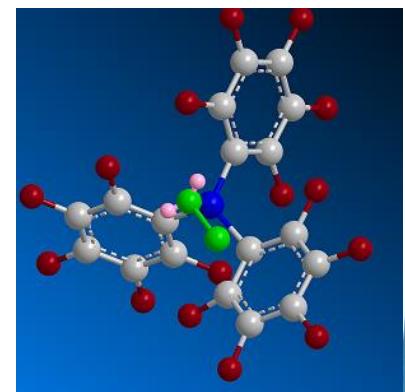
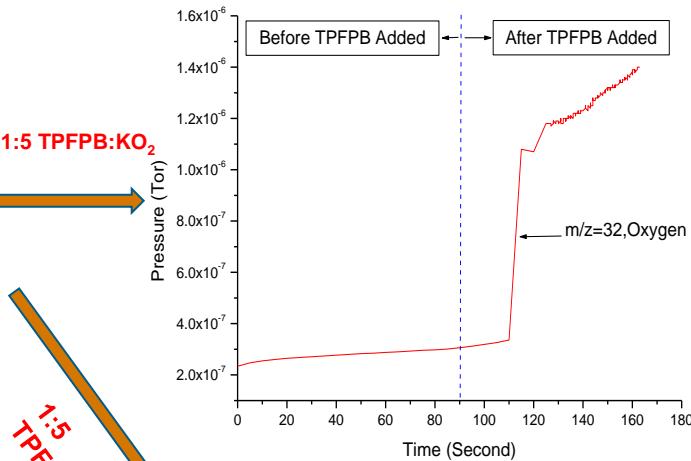
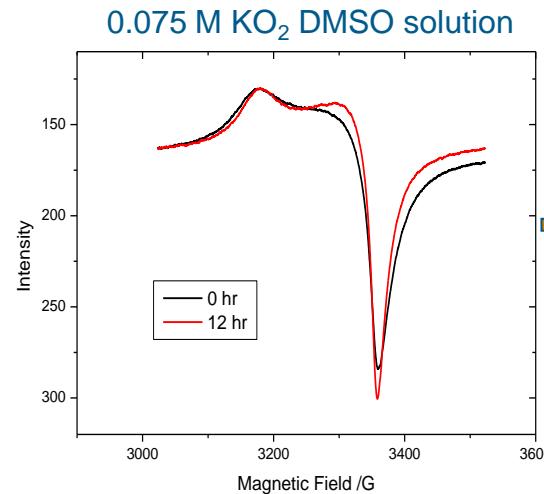
[F. Mizuno, S. Nakanishi, Y. Kotani, S. Yokoishi, and H. Iba, *Electrochemistry*, **78**, 403 (2010).]



P.G. Bruce etc. *J. Am. Chem. Soc.*, 133(2011)8040



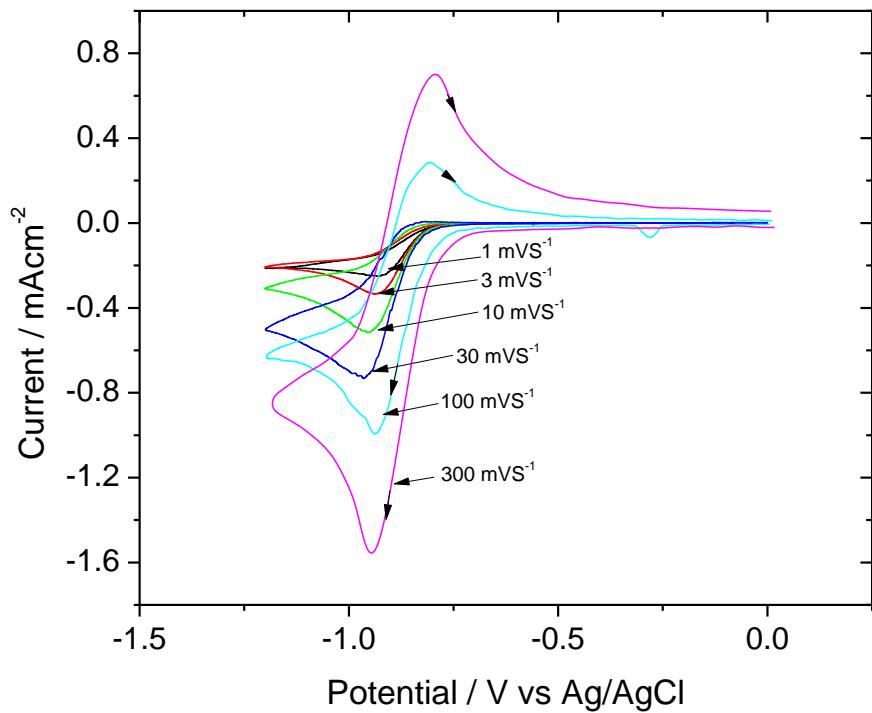
O₂⁻ Indeed Reacts with PC, BUT Catalytic Disproportionation is Much Faster



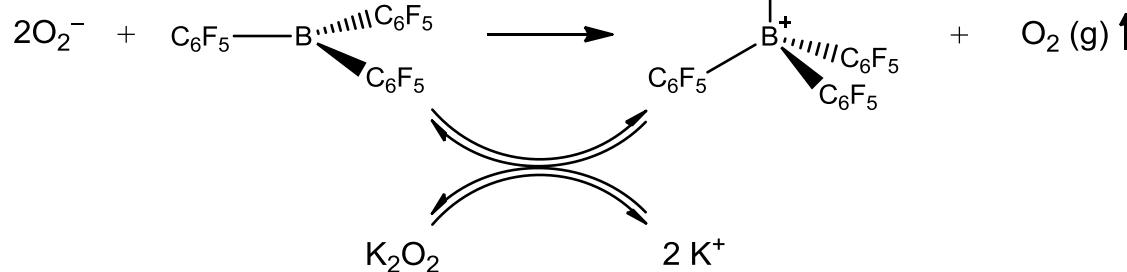
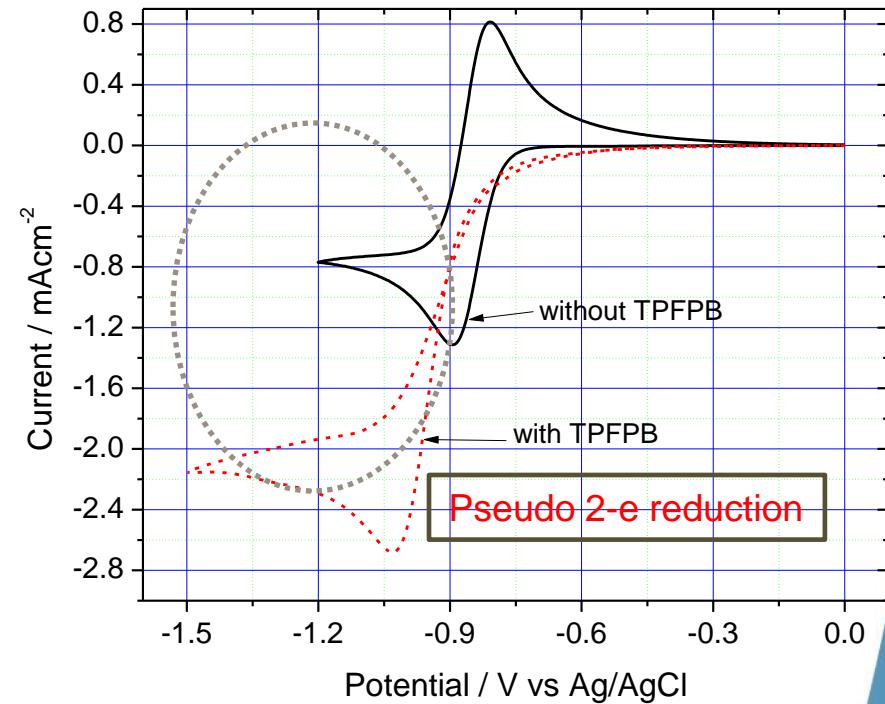
D.Y. Qu etc., Chem. Eur-J 19(2013)8679-8683

Mechanism of Catalytic Disproportionation

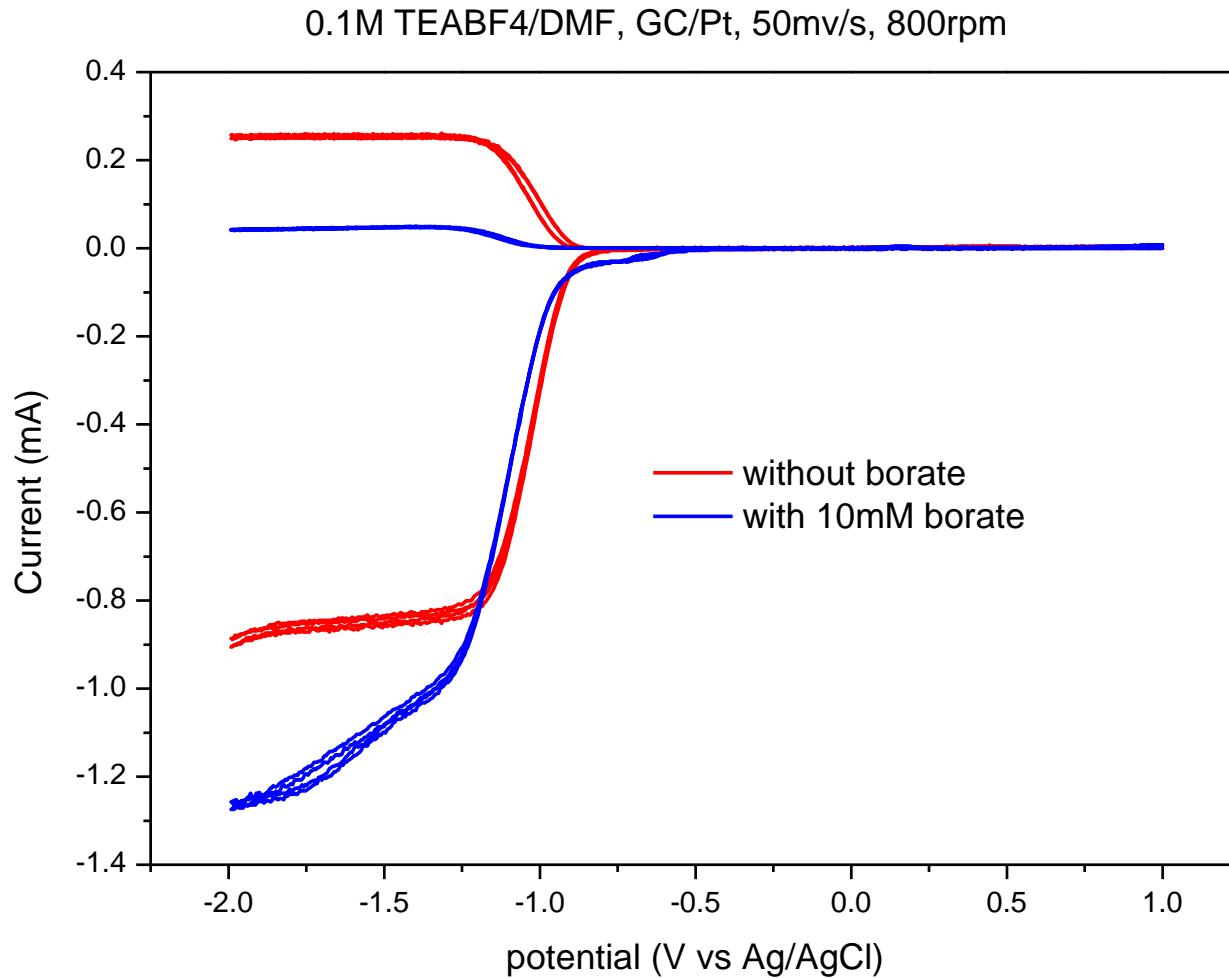
1 M TEABF₄ PC, Glassy Carbon



1 M TEABF₄ acetonitrile, Glassy Carbon

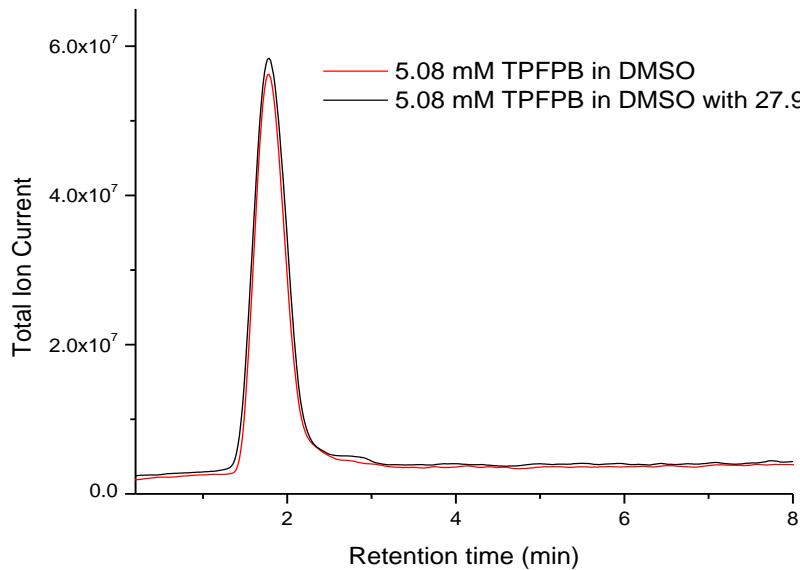


Rotation Ring Disc Electrode



Not published data from Qu's group

TPFPB is a catalyst, not a reactant



Mobile phase: Methanol with 0.01% (v/v) ammonium hydroxide

Figure 1, The chromatogram of TPFPB in DMSO with and without KO₂ obtained by HPLC ESI/MS

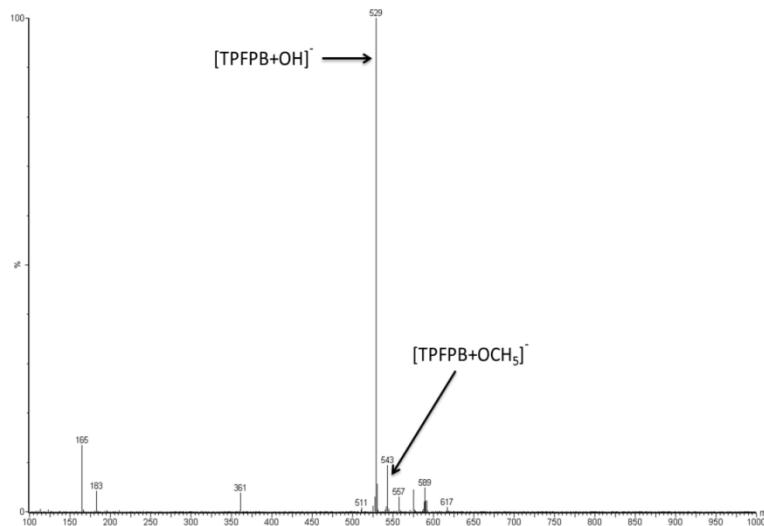
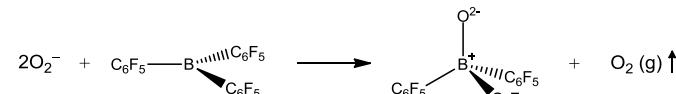
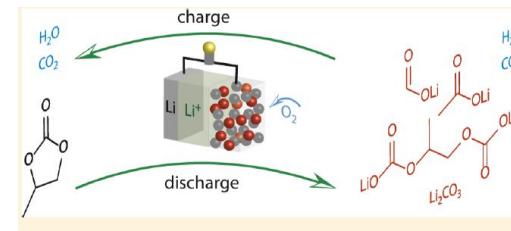
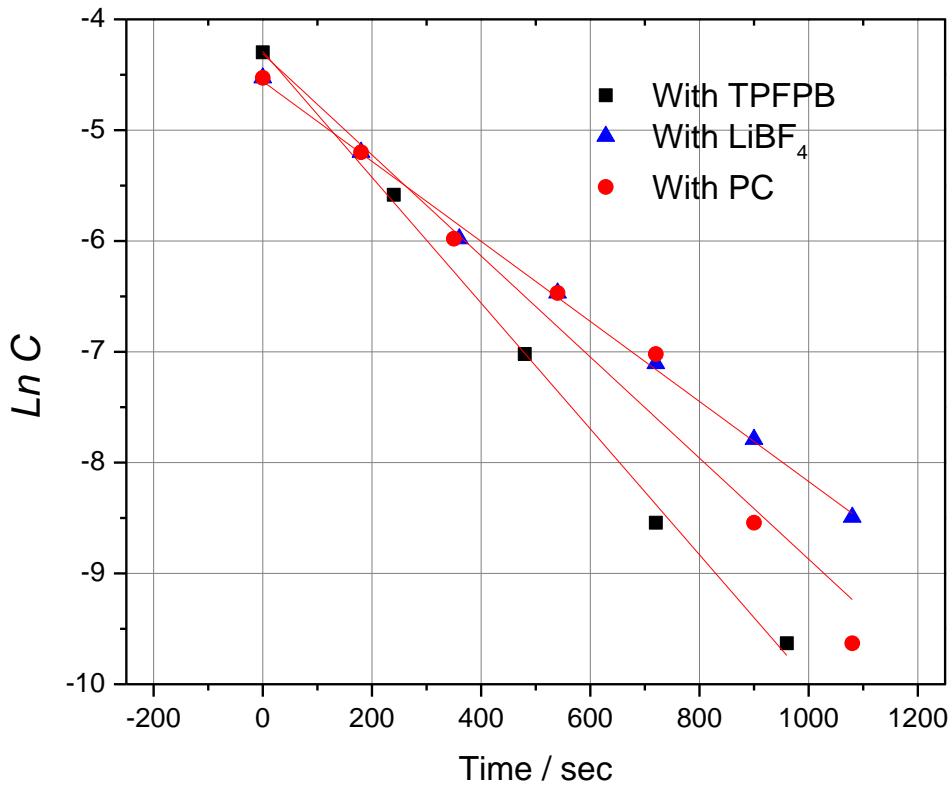


Figure 2, Mass spectrum of TPFPB in ESI(negative)/MS

Kinetic Studies in Comparison of O_2^- Catalytic Disproportionation and Reaction with PC



$$\ln[O_2^-] = \ln[O_2^-]_0 - k't$$

$$k' = [R]k$$

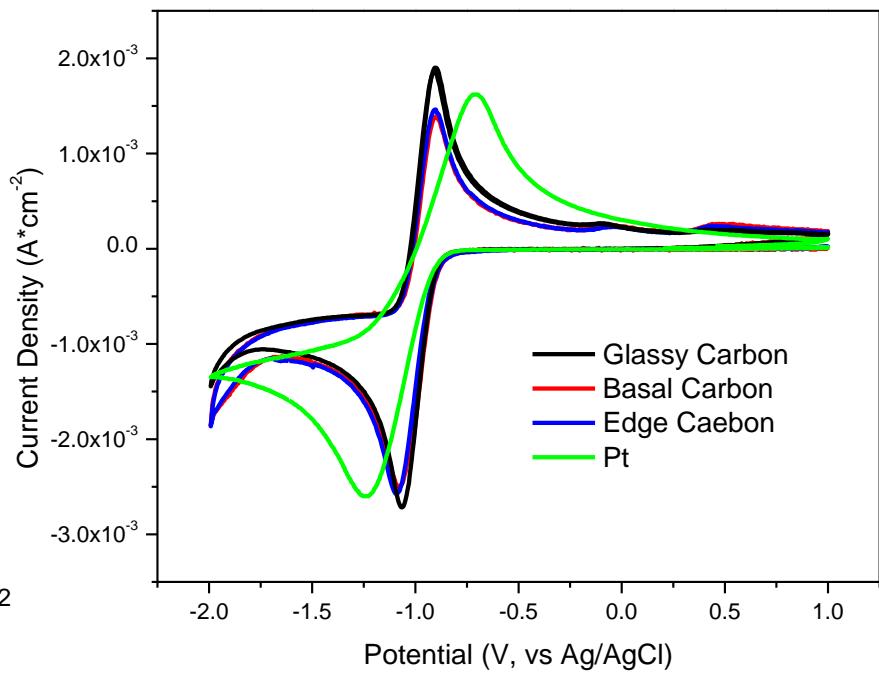
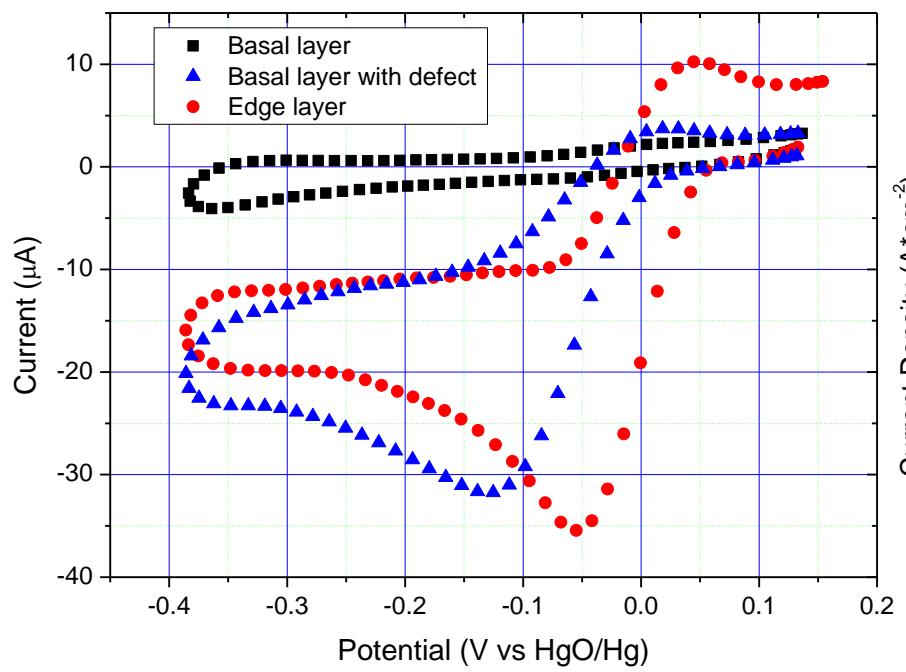
$$k = k'/[R]$$

Table 1: reaction rate constants calculated from table 3. Initial concentration for O_2^- was 0.01 .

	Concentration (M)	STD	R	$k' (s^{-1})$	$K(s^{-1}M^{-1})$
PC	0.08	6.87×10^{-5}	0.998	0.003	0.037
Li ion	0.2	3.78×10^{-4}	0.960	0.004	0.02
TPFPB	0.009	1.59×10^{-4}	0.997	0.006	0.67

Not published data from Qu's group

Catalytic Oxygen Reduction



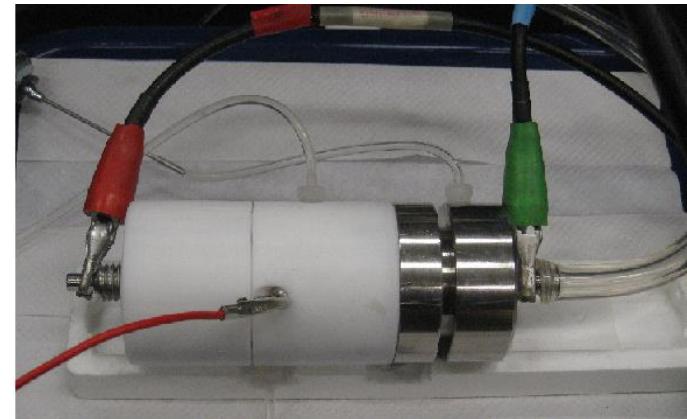
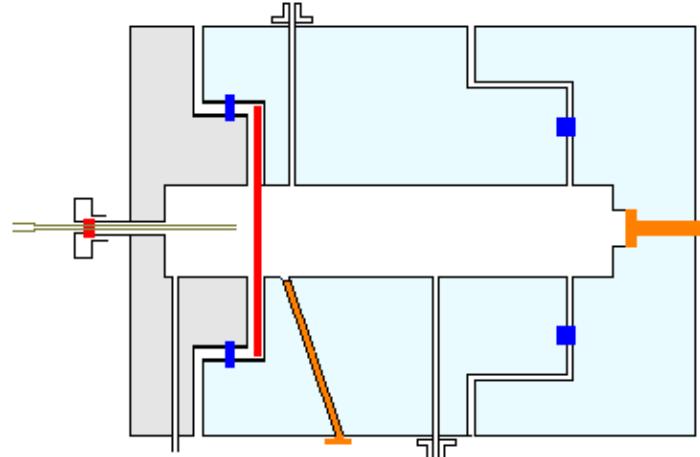
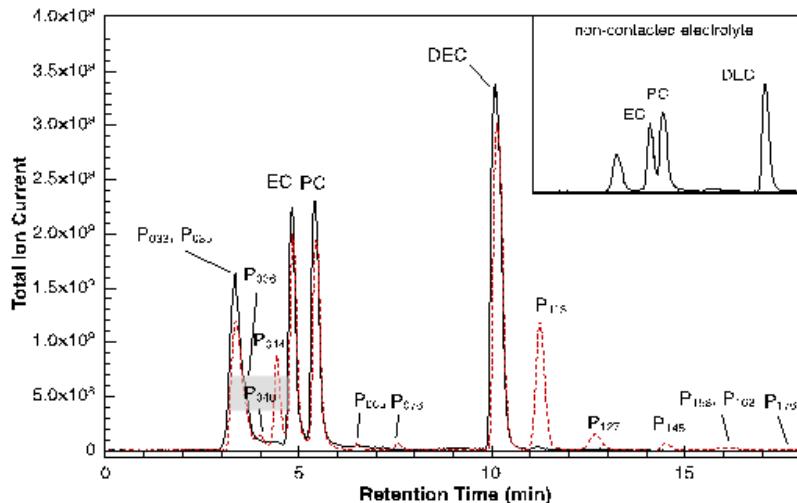
In 30% KOH

D.Qu Carbon 45(2007)1296-1301

In ACN

Not published data from Qu's group

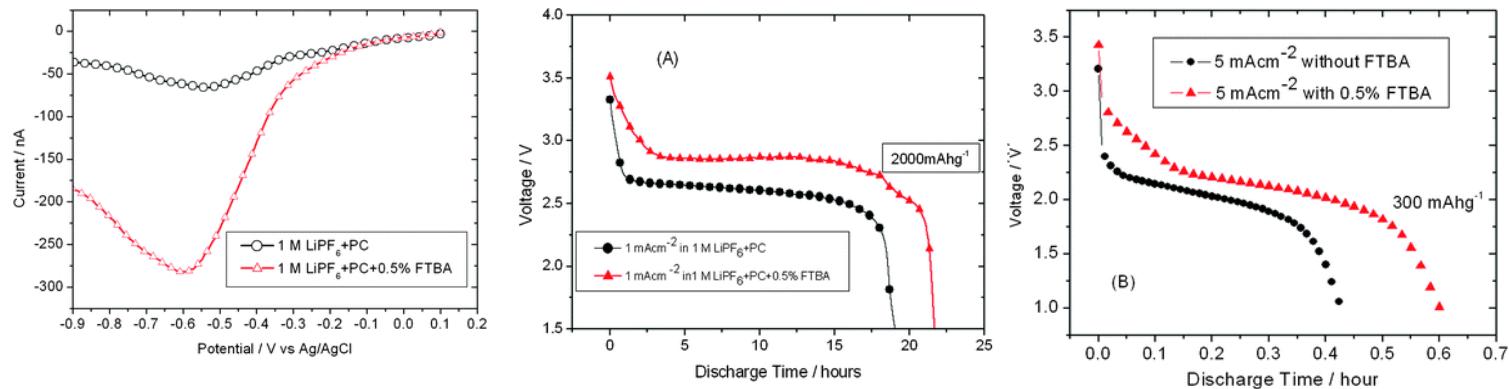
New compounds formed during operation



ID	Empirical Formula	Structure	LogP Calculations			
			XLogP	NC+NHET	ALogP98	KLOP
P ₀₃₅	C ₄ H ₇ O ₃ Li		0.4970	1.4600	-0.0216	0.19
P ₀₃₆	C ₃ H ₄ O ₃		0.5440	1.4600	0.3911	1.01
P ₀₄₀	C ₆ H ₁₀ O ₄		0.6850	1.6800	-0.2366	-0.09
P ₀₄₄	C ₆ H ₁₀ O ₄		0.7340	1.6800	0.1094	0.27
P ₀₆₅	C ₆ H ₁₂ FO ₆ P		0.7500	1.4600	1.5320	0.44
P ₀₇₆	C ₉ H ₁₉ O ₇ P		0.9360	1.5700	0.5417	0.87
P ₁₁₃	C ₉ H ₁₈ O ₅		1.4440	1.2400	1.6345	0.72
P ₁₂₇	C ₁₃ H ₂₆ O ₇		1.5620	1.5700	2.3572	1.15
P ₁₄₅	C ₁₁ H ₂₄ O ₄		1.8060	1.6800	1.1794	1.34
P ₁₅₈	C ₁₀ H ₂₀ O ₅		1.8760	1.9000	1.5110	1.72
P ₁₆₂	C ₁₅ H ₃₂ O ₆		2.3940	2.1200	0.9876	1.25
P ₁₇₆	C ₁₄ H ₂₈ O ₇		2.6740	2.2300	1.4811	1.54

What can we do before find a good catalyst to assist charge transfer? – improve mass transfer.

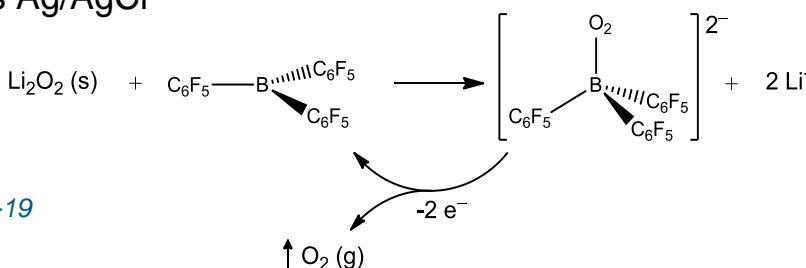
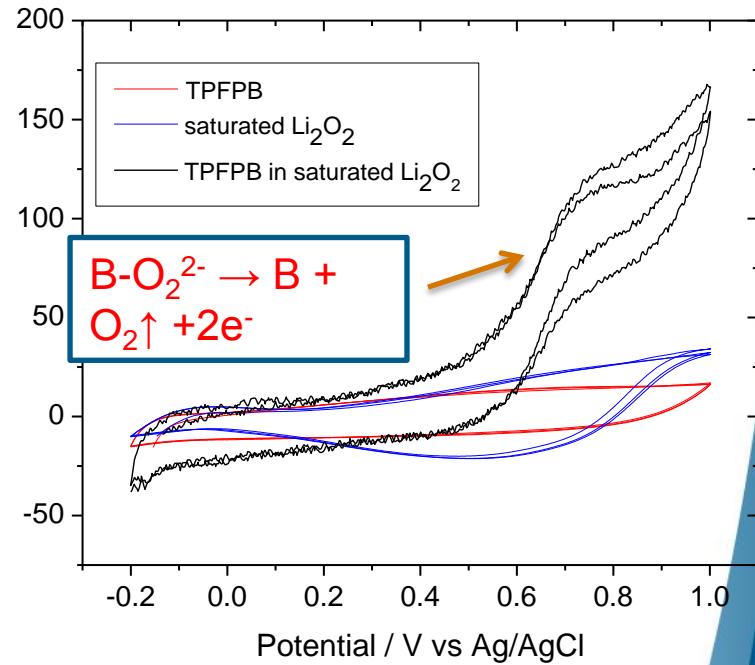
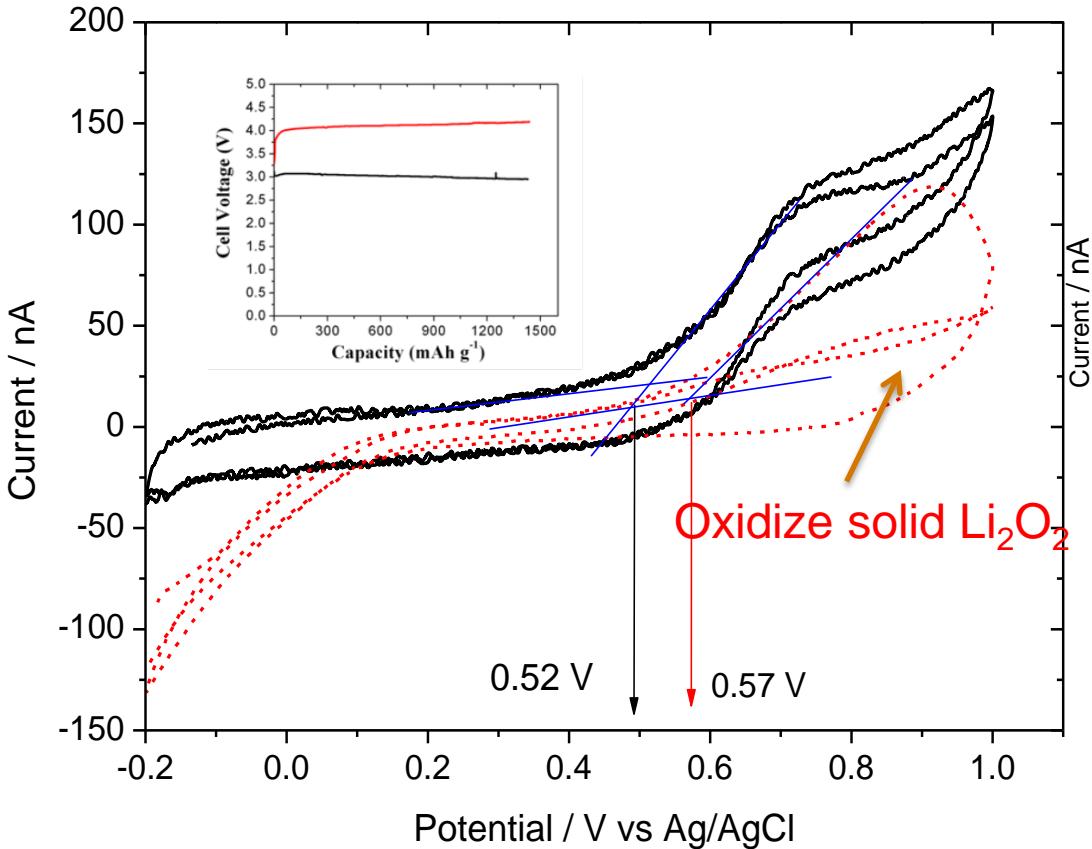
*Increasing Oxygen concentration and diffusion rate in the electrolyte -



D. Qu etc. *Energy Environ. Sci.*, 2011, 4, 3697-3702

Li_2O_2 becomes soluble in Borate additive and the Peroxide complex can be re-oxidized

Catalyst for solid deposit and soluble species.



Conclusions

- ▶ The interaction between superoxide and solvent can be minimized by the catalytic disproportionation of the superoxide. The rate for the disproportionation is substantially faster than that of the interaction.
- ▶ Li_2O_2 becomes soluble with borate additive. The kinetics for the re-oxidation of the soluble B-O_2^{2-} is better than that of solid Li_2O_2 . Therefore the round-trip efficiency is higher.
- ▶ New compounds formed during cell operation, which inevitably poison the catalyst on the GDE .

Acknowledgment

The authors are grateful for the financial support from the Department of Energy, EERE, OVT for the continuous support.